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COMPLETE SPECIFICATION

Improvements relating to the Synthesis of Motor Fuel Hydrocarbons

(A communication from STANDARD OIL DEVELOPMENT COMPANY, a corporation duly organized and existing under the laws of the State of Delaware, United States of America, having an office at Linden, New Jersey, United States of America).

I. JOHN CONRAD ARNOLD, of 29, Southampton Buildings, Chancery Lane, London, W.C.2, a British subject, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The present invention relates to improvements in the art of producing gasoline, and more particularly it relates to improvements in the so-called Fischer-Tropsch synthesis which involves the reaction between carbon monoxide and hydrogen to form hydrocarbons boiling within the gasoline range. The Fischer-Tropsch synthesis to form hydrocarbons from CO and hydrogen is a matter of record. It is usually performed in the presence of a catalyst such as cobalt, promoted by thorium, magnesia and other agents supported on a spacing agent or support such as Kieselguhr or silica gel. Other catalysts are known to be effective. The synthesis is a reaction which is very critical as to temperature. The optimum temperature for it at moderate pressures is about 400° F. and should not vary more than 10° F. from this temperature if good results are to be secured.

It will be appreciated that since the Fischer-Tropsch synthesis is so sensitive and critical as regards temperature conditions that it is a delicate reaction to carry out successfully in large commercial scale installations. The problem of maintaining accurate temperature control within the narrow limits required by the reaction in a large stationary bed of catalyst in which the reaction takes place is a difficult one. It involves expensive and cumbersome heating and cooling equipment to maintain the reactants at the optimum temperature.

In prior Patent No. 568,913 there is

[Price 2/-]

claimed a continuous process for carrying out chemical reactions in the vapor phase wherein the gaseous or vaporised reactants are discharged into an elongated vertical reaction zone of substantially uniform cross-section, the temperature within such zone being maintained within a desired range by the maintenance therein of a body of powdered material which may be either catalytic or inert. the velocity of the gases being regulated so as to maintain substantially the same body of powdered material in the reaction zone in a dense phase suspension of powder in gas with the flow characteristics of a fluid, a powder disengaging zone being provided above such reaction zone in which the velocity of the gas is reduced to permit substantially complete disengagement of the powdered material therefrom, the disengaged material gravitating into such reaction zone.

An application of this process to a Fischer synthesis is briefly described, it being stated that preferred operating conditions are pressures of from 1 to 10 atmospheres, temperatures of from 300° to 500° F., a hydrogen/CO ratio of 2:1 and cobalt on activated clay as a catalyst.

The present invention comprises a process for the synthesis of hydrocarbons of gasoline boiling range from hydrogen and carbon monoxide, wherein a limited weight of a powdered Fischer-Tropsch catalyst is charged to a vertical reaction zone, the hydrogen and carbon monoxide being caused to flow upwardly through the charged catalyst in the reaction zone at a superficial velocity as hereinafter defined of from $\frac{1}{2}$ to 10 ft. per second whereby the catalyst is maintained in a highly agitated, turbulent, ebullient state, an elevated temperature and pressure being maintained in the reaction zone, and the vaporous reaction products being permitted to pass from the mass of catalyst into an expanded disengaging chamber where the velocity of the vapors is sufficiently reduced to permit gravitation of entrained catalyst into the reaction zone, the reaction products substantially free of catalyst being recovered

from the top of the reaction zone, and the temperature of the reactants in the reaction zone being maintained within a desired temperature range by causing a heat abstracting fluid to flow continuously in heat exchange relationship with said mass of catalyst.

The term "superficial" or "net" velocity of the gas or vapor, in this Specification, means the linear gas or vapor velocity which is calculated at the temperature and pressure conditions prevailing at the bottom of the reactor, assuming no catalyst to be present.

The invention will be best understood by reference to the accompanying drawing in which there is shown diagrammatically a preferred modification of the invention.

(1) represents a reactor which is preferably in the form of a vertical cylinder having an upper expanded portion (3) forming a disengaging chamber, for purposes presently to appear. A mixture of preheated hydrogen and carbon monoxide, the mixture containing preferably 2 mols of H_2 to one mol of CO, although lower ratios of hydrogen down to equimolal quantities may be used, is introduced into the reactor through line (5) and flows upwardly through a perforated member (10) which may be a grid plate or a screen inserted to cause distribution of the gases entering the reactor. Within the reactor, there is maintained a mass of catalyst (C) which may be in the form of a powder having a particle size varying from 200—400 mesh and usually such that 90—95% of it has a particle size of 300 mesh. To start operations this catalyst may be fed from a supply hopper (12) through pipe (14) at the same time that the gases enter.

The linear velocity of the gases is maintained within the limits of from $\frac{1}{2}$ to 10 ft. per second, depending on the particle or aggregate size, that is to say, the net or superficial velocity of the gases is maintained within those limits with, however, a velocity of $1\frac{1}{2}$ to 3 ft. per second preferred, where catalyst with 90% less than 300 mesh is used. If, however, particles ranging in size to $\frac{1}{4}$ -inch in diameter are used, the gas velocity is 5 to 10 ft. per second.

The gases cause the powdered catalyst to be "fluidized," that is, to be in the condition previously referred to. This condition or state of the catalyst is not a true suspension, since the velocity of the gases is low enough to permit the catalyst to have motion independent of the general upward direction of the gas. But nevertheless it is supported by the gas or vapors within the reactor, to form

a mass having a density which may vary considerably depending on the density of the particles. The fluidized mass extends from the grid plate (10) to a level (L) in the reactor and, as previously indicated, the particles of catalyst move upwardly and downwardly, sidewise and in all conceivable directions within the limits specified, and the gases eventually entering (3), due to the expanded diameter of the chamber (3), are decreased sufficiently in velocity so that they will no longer support any substantial quantity of catalyst, and therefore the latter entrained in the gases gravitates into (1).

The reaction products substantially depleted of catalyst (except for very fine dust) are withdrawn through line (20) and then are passed usually into a dust collector or electrical precipitator (22) where the last traces of the fines are separated and returned to the reactor through line (25), and the reaction products pass overhead, substantially depleted of catalyst, through line (30), and thereafter they are discharged into scrubbing equipment (35) where they are scrubbed in the usual manner to recover hydrocarbons and thereafter they are processed in a conventional manner to obtain the final product. To accomplish this a scrubbing oil of about 30° A.P.I. gravity is fed to the top of scrubbing tower (35) through line (40). The scrubbing oil and recovered hydrocarbons are removed from tower (35) through line (41) and delivered to distillation equipment (not shown) to recover the desired product. The undissolved gases are withdrawn from the scrubber through line (43). It is considered unnecessary to describe in detail the processing of the synthesized hydrocarbons and unreacted CO and H_2 for these features in our process are old as in the prior art and need not therefore be fully described herein.

Returning again to the heart of the invention which resides in the use of the reactor of the type we have described, it is pointed out that the catalyst remains in the reactor indefinitely since the Fischer synthesis is one in which the catalyst requires no regeneration, by burning off deposits. However, over an extended period of several days the catalyst accumulates a deposit of wax from the synthesis. This is removed by exposing the catalyst to hydrogen or a hydrogen-containing gas or to inert (CO_2 , flue gas, N_2 , etc.) gases heated up to 800° F., the CO or H_2 and CO reactants flow being interrupted during the cleansing period. The catalyst may remain in the reactor for months. When

a new charge of catalyst is desired, the old catalyst is rejected through line (44) and the new catalyst fed through line (14). Since, of course, the reaction is highly exothermic, it will be necessary to abstract heat from the catalyst, and this result is attained by circulating steam or water through a coil (40) which surrounds the outside wall of the reactor.

10 The position and type of cooling surface is not critical; it may be a coil about the reactor, a jacketed reactor, horizontal tubes across the reactor, or coils in a vertical position, with or without extended surface. The only requirement is that the agitated particles contact the cooled surface.

It is pointed out that the foregoing type of operation is to be distinguished from prior art operations in which powdered material was fountained into a pear-shaped reactor where it fanned out at a point removed from the entrance point and gravitated toward the entrance along sloping sides of the reactor. There the catalyst is not thoroughly and uniformly mixed with gaseous or vaporous reaction products. The success of the operation of the invention depends on the formation of a dense phase suspension which at all times is in a turbulent, fluidized, highly agitated state or condition, thoroughly mixed with gaseous reactants at all times.

35 With respect to conditions of temperature and pressure, or feed rates in the reactor, as indicated, my overseas correspondents preferably operate at a temperature of 400° F. in the reactor, plus or minus 10°. This 400° F. temperature is not fixed at this value but is a variable with CO:H₂ ratio of feed, the pressure and the catalyst, but when it is fixed by these factors, the variation in either direction may not exceed 10°.

45 There is preferably maintained a pressure of from 5—150 lbs. per square inch gauge within the reactor and a feed of 1 to 3 mols of hydrogen per mol of CO at a feed rate of from 0.2 to 1 weight of total feed per weight of catalyst per hour. The catalyst itself is cobalt oxide on Kieselguhr, preferably, the amount of cobalt oxide being 30% of the composition by weight. There may also be used iron, iron suspended on silica gel, alumina, and the like, and promoters such as thoria or magnesia increase the efficacy of the process.

60 Having now particularly described and ascertained the nature of the said invention and in what manner the same is to be performed, as communicated to me by

my foreign correspondents, I declare that what I claim is:—

1. A process for the synthesis of hydrocarbons of gasoline boiling range from hydrogen and carbon monoxide, wherein a limited weight of a powdered Fischer-Tropsch catalyst is charged to a vertical reaction zone, the hydrogen and carbon monoxide being caused to flow upwardly through the charged catalyst in the reaction zone at a superficial velocity as hereinbefore defined of from $\frac{1}{2}$ to 10 ft. per second whereby the catalyst is maintained in a highly agitated, turbulent, ebullient state, an elevated temperature and pressure being maintained in the reaction zone, and the vaporous reaction products being permitted to pass from the mass of catalyst into an expanded disengaging chamber where the velocity of the vapors is sufficiently reduced to permit gravitation of entrained catalyst into the reaction zone, the reaction products substantially free of catalyst being recovered from the top of the reaction zone, and the temperature of the reactants in the reaction zone being maintained within a desired temperature range by causing a heat abstracting fluid to flow continuously in heat exchange relationship with said mass of catalyst.

2. A process as set forth in Claim 1, in which the superficial velocity of catalyst through the reaction zone is maintained within the limits of $\frac{1}{2}$ to 3 ft. per second where the particle size is such that 90% will pass through a 300 mesh screen.

3. A process as set forth in Claim 1, in which the main bulk of catalyst remains continuously in the reaction zone and gasiform material is discharged into said zone and withdrawn therefrom substantially free of catalyst material.

4. A process as set forth in Claim 1, in which the reaction temperature at all times during the course of the reaction does not vary by more than $\pm 10^\circ$ F.

5. A process as set forth in Claim 1, in which the process is interrupted periodically to cleanse the catalyst by treatment with a hydrogen-containing gas.

6. A process as set forth in Claim 1, in which the catalyst is cleansed periodically with hot inert gases.

7. A process according to any of the preceding Claims, wherein the catalyst is cobalt oxide on kieselguhr, the cobalt oxide preferably comprising 30% by weight of the composition.

Dated this 8th day of May, 1944.

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Agents for the Applicant.

Reference has been directed, in pursu-
ance of Section 8, sub-section (2), of the
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to Specification No. 568,913.

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